Pentafluorophenyl-Metal Chemistry I

Preparation and Characterization of some Tin Compounds

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Discussion

The differences afforded by complete substitution of fluorine for hydrogen in organic moieties bonded to metals or metalloids have been investigated by a large number of workers. The contrasts between alkyl and perfluoroalkyl derivatives are in many cases well established. In the same way, vinyl and perfluorovinyl derivatives of metals have been compared. Whereas the phenyl derivatives which provide a sp²-hybridized carbon atom bonded to a metal (or metalloid) without labile a-substituted functions have been known for many years, the analogous perfluoro compounds have only recently been reported or still are unknown.

Pentafluorobenzene 1 became available during recent years and its bromo- and iodo-derivatives 2 were found suitable for the preparation of reactive intermediates such as the Grignard and lithio-

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4 L. A. Wall, R. E. Donadio, and W. J. Pummer, J. Amer. chem. Soc. 82, 4846 [1960].
via cleavage reactions of the type effective in Group IIIA chemistry. However, such utility appears limited in contrast to phenyl analogues on the basis of our results and those of others. Pentfluoro-phenyl derivatives of Group IIIA may be more conveniently prepared by direct treatment of MX₃ (X = halogen) with the Grignard reagent.

Several methods for preparing pentafluorophenyltin compounds have been examined. Utilizing a modified Wurtz-type reaction reported for the preparation of perfluorovinyltin compounds, dibutyltin chloride was reacted with bromopentafluorobenzene and magnesium in absolute tetrahydrofuran, but without success. By preparing the Grignard reagent separately and then adding the tin halide, bis-(pentafluorophenyl)-dibutyltin was obtained in a small yield. The yields increased with prolonged reaction time and higher reaction temperature. As bromopentafluorobenzene failed to react with magnesium in butyl ether, however, ethyl ether was employed for the initial preparation of the Grignard reagent. After addition of the tin halide, this solvent was gradually displaced by butyl ether or even toluene. The butyl ether slurries were hydrolyzed and worked up in the usual way by extraction and distillation of the tin derivatives. From recent experience, however, this procedure is simplified by using toluene, from which the magnesium salts are filtered off and the pentafluorophenyltin derivatives isolated directly.

The Table gives the physical properties as well as analytical data for a series of pentafluorophenyltin compounds. These compare very well with the corresponding phenyl analogues, particularly with respect to volatility and solubility. Their infrared spectra do not show any important trends. Several principal absorption bands also are included in the table and are in good agreement with assignments reported for fundamental stretching modes in pentfluoropyridine, pentafluorobenzene and hexafluorobenzene.

Bis-(pentafluorophenyl)-dibutyltin was cleaved with boron tribromide and yielded comparable amounts of butylboron dibromide and pentafluorophenylboron dibromide.

\[
(C_4H_9)_2Sn(C_6F_5)_n + 2 BBBr \rightarrow C_4H_9BBBr_2 + C_6F_5BBBr_2
\]

Under the same conditions tetrakis-(pentafluorophenyl)-tin, however, remained unaffected, although its phenyl analogue is readily cleaved. That such nonreactivity is caused by the significant steric hindrance of the pentafluorophenyl moiety has been suggested.

**Experimental**

Alkyl-, vinyl-, and phenyl-tin halides used in this work were obtained from commercial suppliers and repurified prior to use. Bromopentafluorobenzene was prepared from pentafluorobenzene (Imperial Smelting Corp. Ltd., England) according to literature.

All reactions were conducted in standard glassware, carefully dried and flushed with purified nitrogen. Air-sensitive materials were manipulated in conventional high-vacuum apparatus and an efficient drybox.

As examples of the procedures developed, the reactions of organotin halides with pentafluorophenylmagnesium bromide in either butyl ether or toluene are described.

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13 F. E. Brinckman and F. G. A. Stone, J. Amer. chem. Soc. 82, 6218 [1960].
14 See succeeding Paper Part II, Z. Naturforsch. 20b, 5 [1965], and ref. 11.
16 Using saturated aqueous NH₄Cl. It is of interest to note that under related circumstances these pentafluorophenyltin compounds are rapidly hydrolyzed by catalytic quantities of halide (or cyanide) in alcoholic solution (see ref. 7). The high yields obtained in the present study suggest that conditions for such hydrolysis are very specific.
18 Ultraviolet spectra have been obtained for many of the tin compounds reported herein, A. R. Lawrence, unpublished results.
21 Similarly, BCl₃ cleaves Me₃SnC₆F₅ to give both C₆F₅BCl₂ and MeBCl₂ in unspecified amounts (see ref. 7).
Pentafluorophenylmagnesium bromide

In 100 ml absolute ethyl ether, 1.50 g. (62 mg atoms) magnesium turnings were reacted with 14.70 g. (60 mmoles) bromopentafluorobenzene, which was added over a period of 15–20 minutes causing immediate reaction. Within 2 hours most of the metal had dissolved resulting in a black solution. To assure a complete reaction the Grignard mixture was stirred overnight.

Attempts to clear the solution by filtering failed as only tiny flakes of leftover magnesium were found. Thus the black ether solution of pentafluorophenylmagnesium bromide was conveniently used as prepared. From concentrated ether solutions the Grignard reagent sometimes precipitated as a black salt, but re-dissolved on addition of ether. Pentafluorophenylmagnesium bromide also can be readily prepared in tetrahydrofuran. In butyl ether, however, the Grignard reactions does not proceed without addition of an equal amount of ethyl ether, whereupon it starts slowly.

Bis-(pentafluorophenyl)-divinyltin

Over a period of 10 minutes 6.10 g. (25 mmoles) divinyltin dichloride (b.p. 62°/2.5 mm) was added dropwise to an ether solution (100 ml) containing 50 mmoles pentafluorophenylmagnesium bromide. Considerable heat of reaction was detected and a black oil separated. The reaction mixture was refluxed and after 1 hour the ethyl ether gradually was displaced by addition of butyl ether. At about 70° the black oil disappeared and at about 130° a gray salt precipitated with the solution becoming light brown. Reflux was maintained at 145° for 2 hours.

On cooling, the mixture was hydrolyzed with excess saturated aqueous ammonium chloride solution. The tin compound was extracted with n-hexane. Removal of the solvents and vacuum fractionation afforded 9.46 g. (75%) of a colorless liquid, b.p. 107°–109°/0.3 mm. Analytical data for bis-(pentafluorophenyl)-divinyltin are incorporated in the table.

Tetrahis-(pentafluorophenyl)-tin

At room temperature a solution of 5.21 g. (20 mmoles) tin tetrachloride in 30 ml absolute n-hexane was added slowly to an excess of pentafluorophenylmagnesium bromide in ether. A vigor-
ous reaction was observed. Reflux was started and within 3 hours, the ether was distilled off by displacement with butyl ether, and reflux was maintained for 3 hours at 145°.

The main portion of the solvent was distilled off before the remaining slurry was hydrolyzed with ammonium chloride solution.

White needles formed in both layers. By addition of methanol a uniform solvent phase was formed from which the crude tin derivative easily could be filtered off. Recrystallization from carbon tetrachloride gave 13.48 g. (85.5%) tetrakis-(pentafluorophenyl)-tin, m. p. 219° — 221°.

**Pentafluorophenyltrimethyltin**

While stirring an ether solution (75 ml) containing 25 mmoles pentafluorophenylmagnesium bromide, 6.09 g (25 mmoles) trimethyltin bromide was added. After 1 hour reflux was started. Within an hour ethyl ether was distilled off with gradual replacement by absolute toluene. At about 105° a gray solid precipitated. Reflux was maintained for another hour.

All salts were filtered from the hot toluene solution. Removal of the toluene and vacuum fractionation yielded 4.95 g. (60%) pentafluorophenyltrimethyltin, b. p. 118° — 119°/50 mm.

**Cleavage of Bis-(pentafluorophenyl)-dibutyltin**

Under inert conditions 12.10 g. (21.3 mmoles) bis-(pentafluorophenyl)-dibutyltin was treated with 11.80 g. (47.5 mmoles) boron tribromide. Immediately a yellow color was observed, which turned to red within 30 minutes. After 3 hours of reflux (95°), the red color had disappeared and a white solid separated out. All volatile material was distilled off, leaving a gray residue.

Fractionation of the condensed liquid afforded 3.45 g. (35.5%) somewhat unstable butylboron dibromide, b. p. 54° — 61°/20 mm and 3.55 g. (22%) pentafluorophenylboron dibromide, b. p. 85° — 88°/20 mm.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Calc.</th>
<th>Found (by hydrolysis)</th>
</tr>
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<tbody>
<tr>
<td>C₄H₉Br₂</td>
<td>Br 70.18</td>
<td>72.07</td>
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<tr>
<td>C₆F₅Br₂</td>
<td>C 21.34</td>
<td>F 28.13</td>
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<tr>
<td></td>
<td>found</td>
<td>C 21.57</td>
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</tbody>
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**Attempted Cleavage of Tetrakis-(pentafluorophenyl)-tin**

No significant change was noted when 7.86 g. (10 mmoles) tetrakis-(pentafluorophenyl)-tin was treated with 2 ml (21 mmoles) boron tribromide and refluxed for 24 hours under nitrogen. After this an additional 0.3 ml boron tribromide in 8 ml absolute n-hexane was added. Following another 24 hours reflux all volatile material was distilled off. A gray residue remained, from which 7.5 g. (95%) of tetrakis-(pentafluorophenyl)-tin could be recovered by sublimation.

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